

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 May 2003 (01.05.2003)

PCT

(10) International Publication Number
WO 03/035714 A1

(51) International Patent Classification⁷: **C08G 61/12,**
C07D 333/20

Madingley Rise, Cambridge, Cambridgeshire CB3 0TX
(GB).

(21) International Application Number: PCT/GB02/04723

(74) Agent: **SHADE, Matthew**; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB).

(22) International Filing Date: 18 October 2002 (18.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0125620.5 25 October 2001 (25.10.2001) GB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): **CAMBRIDGE DISPLAY TECHNOLOGY LIMITED** [GB/GB]; Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **TOWNS, Carl** [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB). **MCKIER-NAN, Mary** [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB). **O'DELL, Richard** [GB/GB]; Cambridge Display Technology Limited, Greenwich House, Madingley Road,

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/035714 A1

(54) Title: TRIARYLAMINE CONTAINING MONOMERS FOR OPTOELECTRONIC DEVICES

(57) Abstract: Monomers having the formula X1-Ar1-[triarylamine]-Ar2-X2 wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups and wherein X1 and X2 are the same or different polymerisable groups and wherein Ar1 and Ar2 are the same or different substituted or unsubstituted aryl or heteroaryl groups. Polymers and copolymers comprising such monomers are also described. The polymers have particular application in organic optoelectronic devices such as organic electroluminescent devices and organic photovoltaic devices.

TRIARYLAMINE CONTAINING MONOMERS FOR OPTOELECTRONIC DEVICES

The present invention relates to triarylamine based trimer monomers and to low band gap polymers and copolymers prepared therefrom and in particular to optoelectronic devices such as electroluminescent devices and photovoltaic devices comprising such polymers and copolymers.

Background of the Invention

Semiconductive organic polymers have been known for several decades, during the past ten years they have seen increasing application in the field of electroluminescent devices, see for example WO90/13148. A typical electroluminescent device comprises an anode, a cathode and a layer of light-emitting material situated between the anode and the cathode, further layers may also be introduced to improve charge injection into the device or charge transport through the device. Semiconductive organic polymers may act as the light-emitting component or as charge transport or charge injecting components in electroluminescent devices. More recently semiconductive organic polymers have found application in photovoltaic devices, as disclosed in WO96/16449, and also as photoconductors and photodetectors.

The nature of the polymeric material used in electroluminescent devices is critical to the performance of the device, materials used include poly(phenylenevinylenes), as disclosed in WO90/13148, polyfluorenes, as disclosed in WO97/05184, poly(arylamines), as disclosed in WO98/06773. In particular copolymers and blends of polymers have been found to be useful in such devices, as disclosed in WO92/03490, WO99/54385, WO00/55927 and WO99/48160. Poly(arylamines) have been disclosed in which the aromatic groups may comprise heteroaromatic moieties such as triazine, see WO01/49769.

Recently there have been efforts to increase the range of available semiconductive polymers and, in particular, to provide polymers with lower band gaps, see WO01/49768. The band gap is the difference in energy levels between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Low band gap materials emit light at longer wavelengths i.e. towards the red

end of the visible region of the electromagnetic spectrum and are also promising candidates for polymeric photovoltaic devices. WO01/49768 discloses a range of low band gap polymers comprising heterocyclic moieties such as benzothiadiazole. Benzothiadiazole is a functional group characterised by its light-emitting and electron transporting properties.

Summary of the Invention

It is an object of the present invention to provide a range of low band gap polymers and copolymers which give efficient emission of light and have utility as hole-transporting components in optoelectronic devices. The invention provides a range of monomers which may be polymerised to provide low band gap polymers and copolymers, the invention further provides optoelectronic devices comprising said polymers and copolymers and methods for the polymerisation of said monomers.

In a first embodiment the present invention provides monomers having the formula



wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups, said groups being the same or different,

wherein X_1 and X_2 are the same or different polymerisable groups,

wherein Ar_1 and Ar_2 are the same or different substituted or unsubstituted aryl or heteroaryl groups.

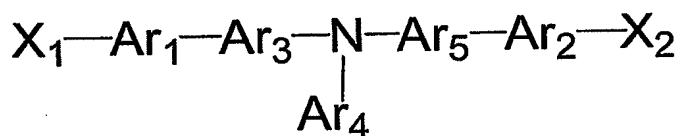
For the purpose of the present invention the term the backbone of the monomer is taken to mean that linear chain to which all other chains may be regarded as being pendant, i.e. that part of the monomer which will be situated in the backbone of the eventual polymer. The backbone is sometimes also referred to as the main chain.

In a more preferred embodiment groups Ar_1 and Ar_2 are heteroaromatic groups such as thiophene, pyrrole, furan or pyridine, thiophene is particularly preferred. Polymerisable groups X_1 and X_2 are preferably selected from the group comprising Cl, Br, I, boronic acids, boronic esters or boranes. In a preferred embodiment polymerisable groups X_1 and X_2 are selected from the group comprising Br and boronic esters.

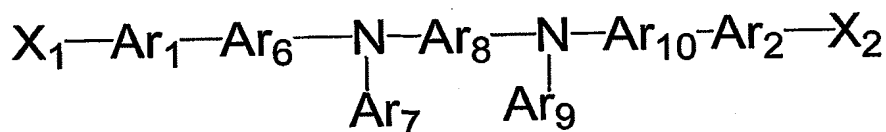
The groups Ar_1 and Ar_2 may be substituted with moieties selected from the group comprising aryl, alkyl, cycloalkyl and alkoxy.

The triarylamine group may comprise a heteroaryl group, this may be either in the chain of the monomer or pendant to the monomer, examples of heteroaryl groups are pyridine, and triazine. In a preferred embodiment the triarylamine comprises a triazine group. The triarylamine group comprises at least one nitrogen, in preferred embodiments the triarylamine group comprises one or two nitrogens.

Particularly preferred monomers are those having the structural formula



wherein X_1 and X_2 are the same or different polymerisable groups and wherein Ar_1 , Ar_2 , Ar_3 , Ar_4 and Ar_5 are the same or different substituted or unsubstituted aryl or heteroaryl groups. Or those monomers having the structural formula

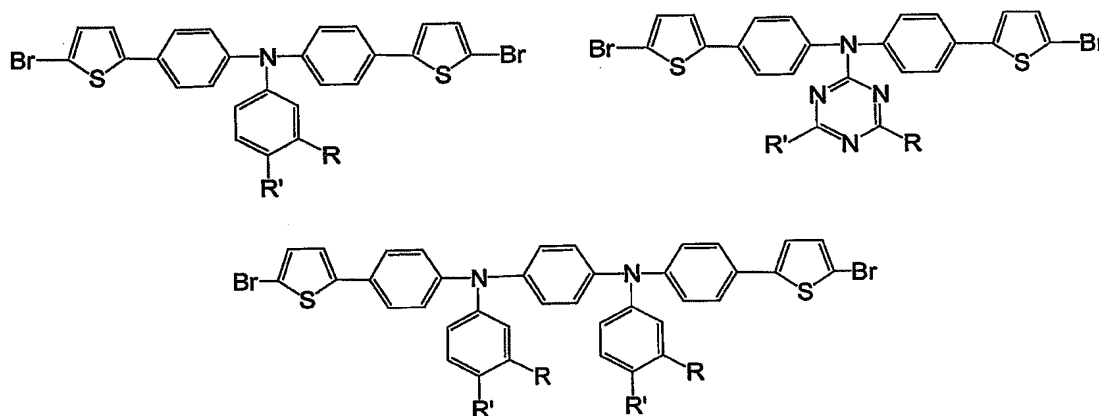


wherein X_1 and X_2 are the same or different polymerisable groups and wherein Ar_1 , Ar_2 , Ar_6 , Ar_7 , Ar_8 , Ar_9 , Ar_{10} are the same or different substituted or unsubstituted aryl or

heteroaryl groups. Examples of groups Ar₁, Ar₂, Ar₃, Ar₄, Ar₅, Ar₆, Ar₇, Ar₈, Ar₉, and Ar₁₀ include such groups as phenylene, thiophene, pyrrole, furan, pyridine and biphenylene.

The aryl or heteroaryl groups Ar₃, Ar₄, Ar₅, Ar₆, Ar₇, Ar₈, Ar₉, and Ar₁₀ may be substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl. Preferred substituents are butyl and sec-butyl.

Particularly preferred monomers according to the present invention include



wherein R and R' are selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl., preferably and R and R' are selected from the group comprising butyl and sec-butyl.

The present invention provides polymers obtainable by the polymerisation of the monomers of the present invention. The present invention also provides copolymers obtained by the polymerisation of monomers of the present invention with suitable comonomers, preferred comonomers are those selected from the group comprising fluorenes, benzothiadiazoles, phenylenes, triarylamine, quinoxalines and stilbenes, preferably said comonomers are fluorenes, benzothiadiazoles, phenylenes or triarylamine.

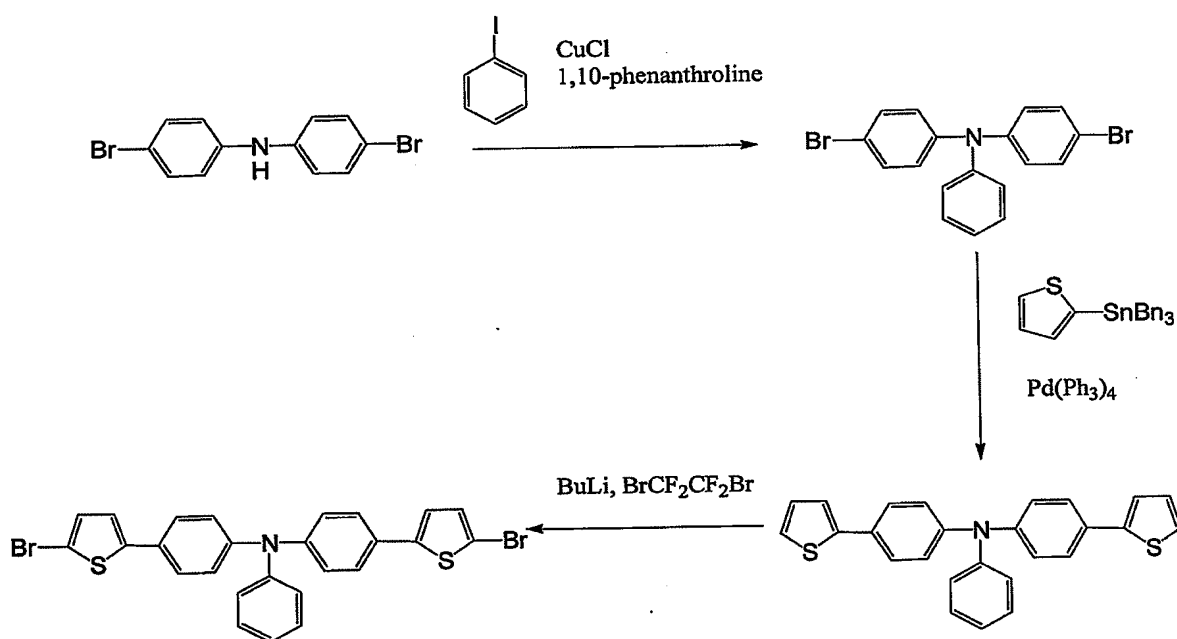
In a further embodiment the present invention provides an optoelectronic device comprising the polymers or copolymers of the present invention. In preferred embodiments said optoelectronic device is an electroluminescent device or a photovoltaic device.

The present invention provides a process for preparing the inventive polymers comprising polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and a monomer according to claim 1 having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX₃-anionic groups, wherein X is independently selected from the group consisting of F and OH.

The present invention provides a process for preparing the inventive copolymers which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and one or more comonomers having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having at least two reactive halide functional groups, and one or more comonomers having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group; or at least (c) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group and one or more comonomers having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX₃-anionic groups, wherein X is independently selected from the group consisting of F and OH.

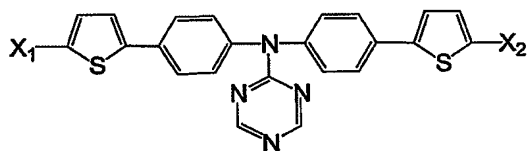
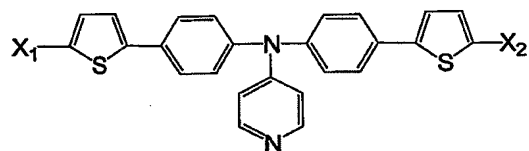
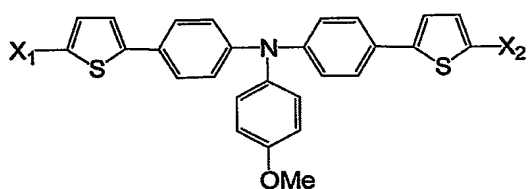
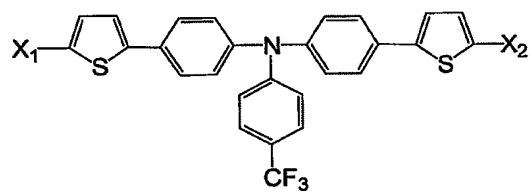
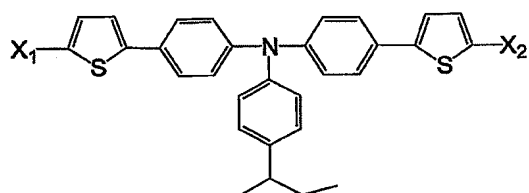
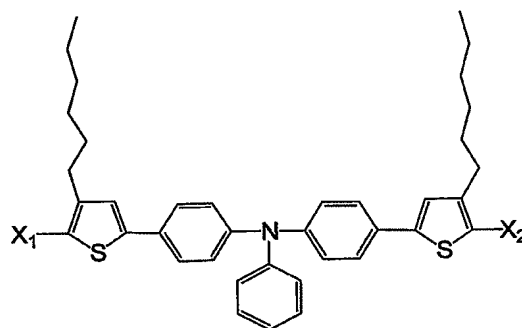
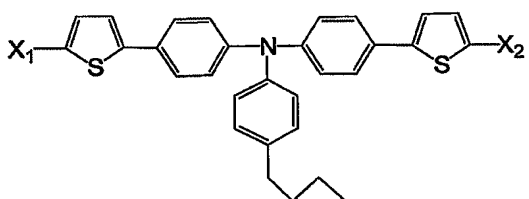
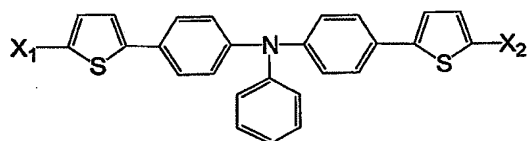
Detailed Description of the Invention

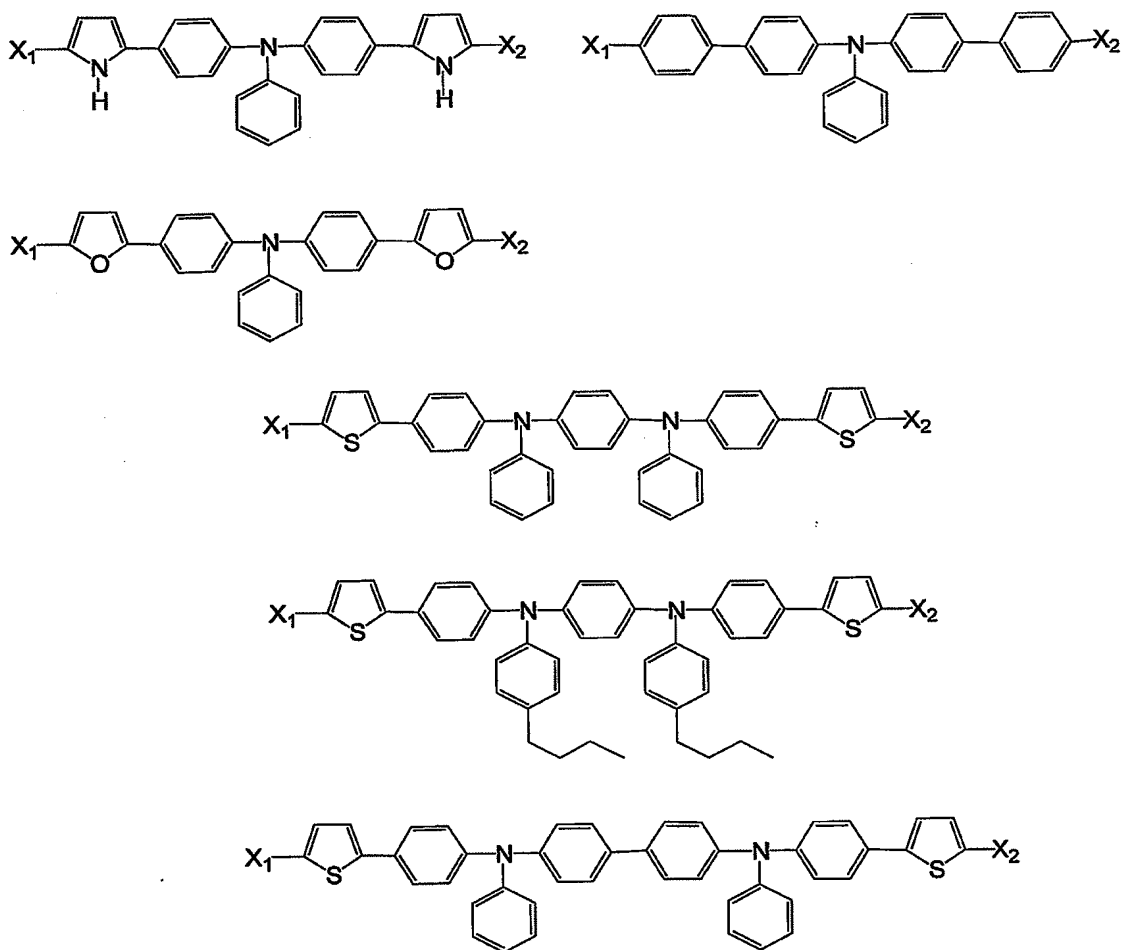
Monomers according to the invention can be prepared by any suitable route known to those skilled in the art. A preferred route involves Ullmann condensation to afford the amine units and Stille coupling to connect the amine units to further aryl or heteroaryl groups. An example of a typical synthetic route is shown



In the above scheme a triarylamine is formed by Ullmann condensation of a diamine and an aromatic iodide, this condensation is generally carried in an inert solvent in the presence of a catalyst such as copper powder, cuprous oxide, cuprous chloride, cuprous bromide, cuprous iodide or cuprous sulfate, 1,10-phenanthroline is added to expedite the reaction. Stille coupling is a common method of coupling aromatic units to heteroaromatic units, in the above scheme the electrophile substituted triarylamine is reacted with an organotin reagent in the presence of a palladium catalyst. Modifications of both Ullmann condensation and Stille coupling are well known to those in the art.

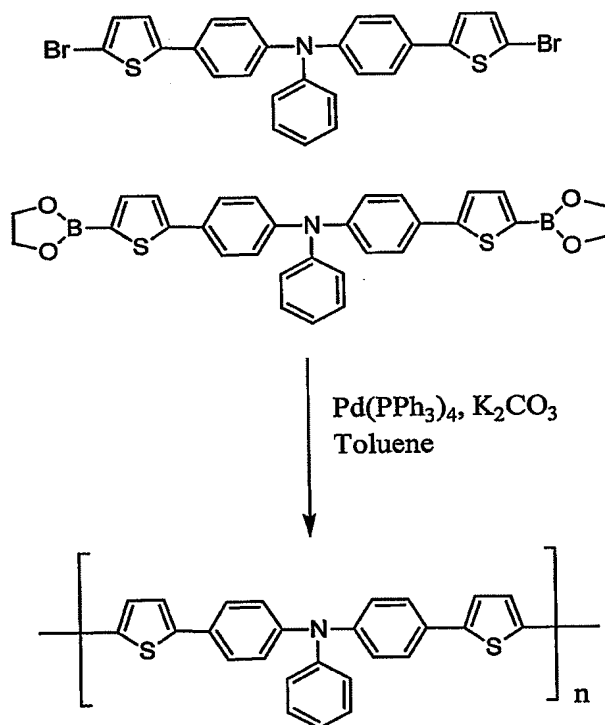
Examples of monomers according to the present invention include those having the following structural formulae





Polymers and copolymers according to the present invention may be prepared by any suitable method known to those skilled in the art, such as Yamamoto or Suzuki coupling, Suzuki coupling is preferred. In the case of monomers with thiophene or pyrrole substituents polymers and copolymers may be prepared by electrochemical polymerisation. Generally, in order to prepare a polymer by Suzuki coupling a suitably substituted monomer is polymerised in a solvent in the presence of a catalyst and a base. Suitable monomers are those comprising, for example, one polymerisable Br moiety and one polymerisable boronic ester moiety, alternatively the reaction mixture may comprise two monomers, one having, for example Br substituents and the other

having, for example, boronic ester substituents. The catalyst is a palladium catalyst such as tetrakis(triphenylphosphine)palladium, suitable bases include alkali or alkaline earth carbonates and alkali or alkaline earth bicarbonates or organic bases such as those disclosed in WO00/53656. The solvent is preferably one in which the polymer is soluble, for example suitable solvents include anisole, benzene, ethylbenzene, mesitylene, xylene and toluene. A typical reaction scheme for Suzuki polymerisation is shown below.

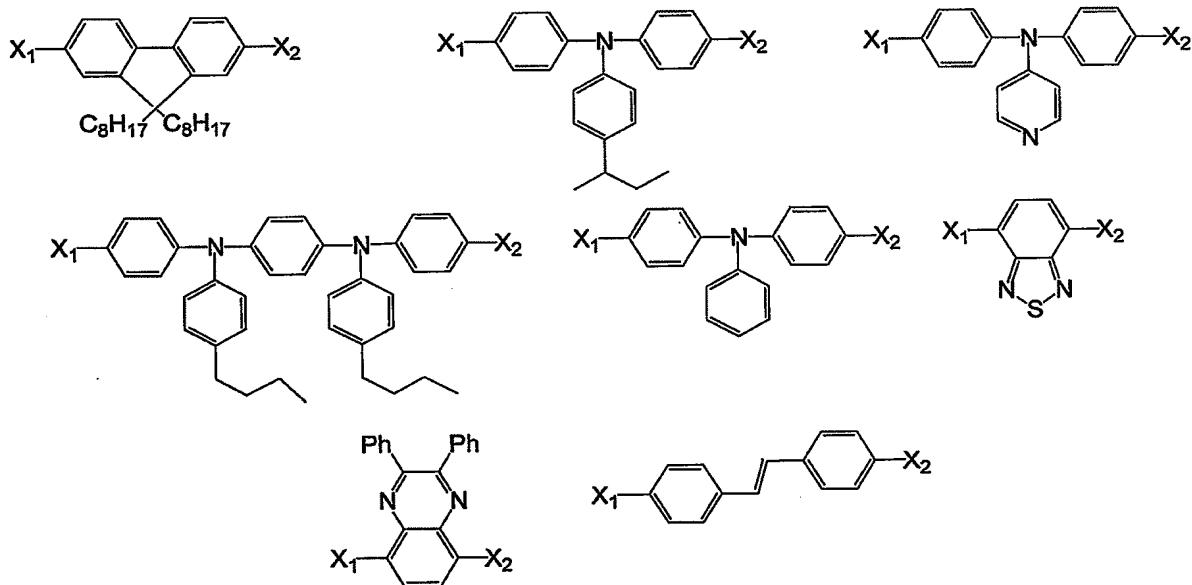


Similarly copolymers according to the present invention may be prepared by Yamamoto or Suzuki coupling, Suzuki coupling is preferred. Generally, in order to prepare a copolymer by Suzuki coupling suitably substituted monomers are polymerised in a solvent in the presence of a catalyst. Suitable reactants for the preparation of a two component copolymer are monomers having at least two boronic ester groups and second monomers having at least two Br groups alternatively monomers having one Br group and one boronic ester group and second monomers having one Br group and one

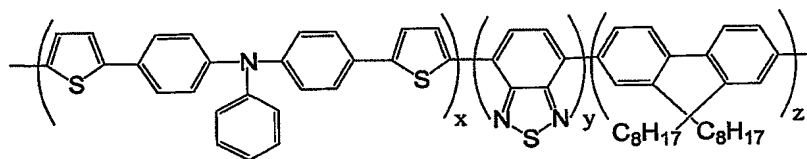
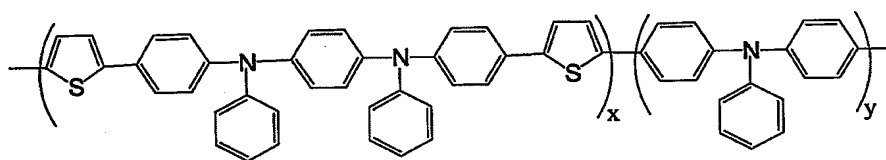
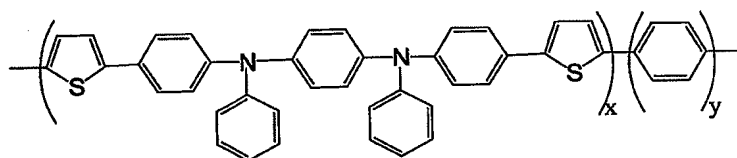
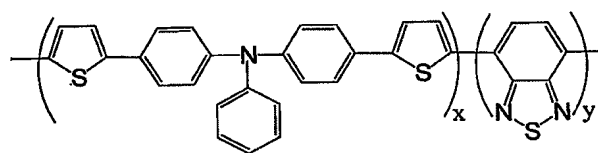
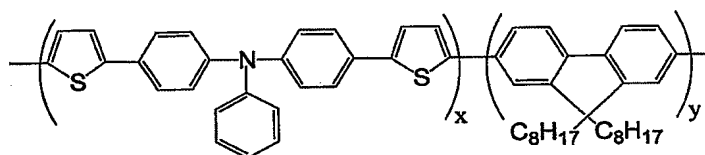
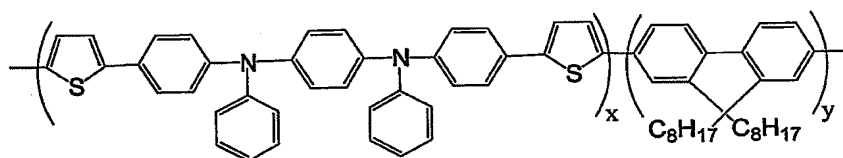
boronic ester group. Clearly terpolymers and higher copolymers could be prepared by reacting suitable monomers. The catalyst is a palladium catalyst such as tetrakis(triphenylphosphine)palladium, suitable bases include alkaline earth carbonates and alkaline earth bicarbonates or organic bases such as those disclosed in WO00/53656. The solvent is preferably one in which the polymer is soluble, for example suitable solvents for polyfluorenes include anisole, benzene, ethylbenzene, mesitylene, xylene and toluene.

End-capping reagents may be added to terminate the reaction or may be added after termination of the reaction. Examples of suitable end-capping reagents include phenylboronate and bromobenzene.

Examples of comonomers which may be copolymerised with the monomers of the present invention to form copolymers include the following, wherein X_1 and X_2 are polymerisable groups.



Examples of polymers and copolymers include those having the following structural formulae, wherein x , y and z represent the proportion of monomers in the copolymer.



The polymers and copolymers of the present invention may be used in optoelectronic devices such as electroluminescent devices and photovoltaic devices. An electroluminescent device according to the present invention typically comprises, on a suitable substrate, an anode, a cathode and a layer of light-emitting material positioned between the anode and the cathode. Electroluminescent devices may further comprise charge transport layers and/or charge injecting layers positioned between the light-emitting material and the anode or cathode as appropriate. In electroluminescent devices of the present invention the polymers or copolymers of the present invention may be present either as the light-emitting layer or as charge transporting or charge injecting layers or alternatively as charge transporting components in a blend with a light emitting material or as light emitting components in a blend with a charge transporting material. The thickness of the emitting layer can be in the range 10nm-300nm, preferably 50nm-200nm. In particular the polymers and copolymers of the present invention may act as hole-transporting layers or as hole-transporting components in a blend.

The anode of the device preferably comprises a material of high work function deposited on a substrate. Preferably the material has a work function greater than 4.3eV, examples of such materials include indium-tin oxide (ITO), tin oxide (TO), aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide and metals such as Au, Ag, Ni, Pd and Pt. Suitable substrates include glass and plastics, the substrate may be rigid or flexible, transparent or opaque. The material of high work function is suitably deposited on the substrate to form a film of 50nm to 200nm, preferably said film has a sheet resistance of 10-100 Ohm/square, more preferably less than 30 Ohm/square.

The cathode of the device is preferably a material of low work function, preferably of work function less than 3.5eV. Examples of such materials include Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Yb, Sm and Al. The cathode may comprise an alloy of such metals or an alloy of such metals in combination with other metals, for example the alloys MgAg and LiAl. The cathode preferably comprises multiple layers, for example Ca/Al or LiAl/Al. The device may further comprise a layer of dielectric material between the cathode and the emitting layer, such as is disclosed in WO 97/42666. In particular it is preferred to use an

alkali or alkaline earth metal fluoride as a dielectric layer between the cathode and the emitting material. A particularly preferred cathode comprises LiF/Ca/Al, with a layer of LiF of thickness from 1 to 10nm, a layer of Ca of thickness of 1 to 25nm and a layer of Al of thickness 10 to 500nm.

Where the electroluminescent device comprises further charge injecting or charge transporting materials, these further materials may be present as separate layers or in a blend with the light emitting material. Examples of suitable charge transporting materials include polystyrene sulfonic acid doped polyethylene dioxythiophene (PEDOT-PSS), polyaniline with anionic dopants such as polymeric anionic dopants, and triaryl amines, including polymeric triaryl amines such as poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) BFA. The charge transport or charge injecting layers suitably have a thickness in the range 10nm to 200nm, preferably 1nm to 50nm.

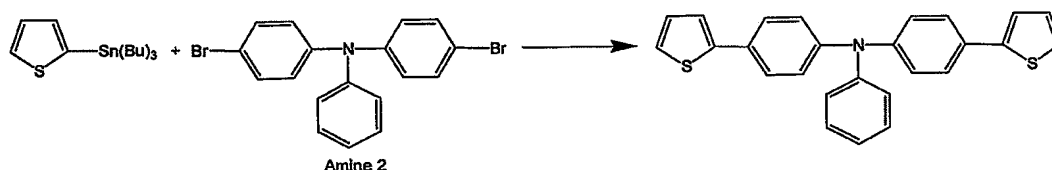
A preferred structure of an electroluminescent device comprises a glass substrate, an ITO anode, a charge transporting layer of PEDOT-PSS, a layer of light-emitting material, a thin layer of LiF and a cathode comprising a layer of calcium and a layer of aluminum.

A photovoltaic device according to the present invention typically comprises two electrodes and situated between said two electrodes at least two semiconductive polymers having different electron affinities, one of said semiconductive polymers being a polymer according to the present invention. The semiconductive polymers may be in the form of a blend or may form separate layers, preferably said semiconductive polymers are in the form of a blend. Generally one of the electrodes comprises a material of high work function, such as ITO, other examples of suitable high work function materials are given above. Generally the other electrode comprises a material of low work function such as Al, other examples of suitable low work function materials are given above. Photovoltaic devices may comprise further charge injection and/or charge transport layers as appropriate, for example a layer of PEDOT/PSS may be included between the anode and the polymeric layer to aid hole transport and injection. Examples of such photovoltaic devices are disclosed in WO99/49525 and US5670791.

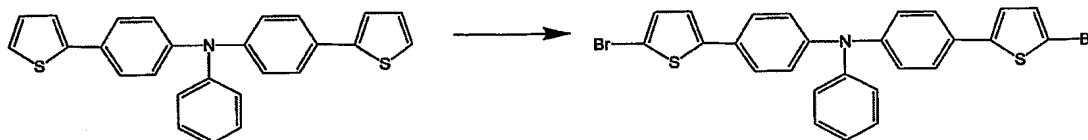
Polymers according to the present invention may also be used as the active component in photodetectors and photoconductors. In a photodetector the polymer is comprised in a layer of organic material situated between two electrodes, a voltage is applied across the layer of organic material and a current detecting circuit is used to measure the current generated due to incident light falling on the organic material. A photoconductor comprising a polymer of the present invention operates along similar lines but comprises a circuit to measure the change in resistance across the polymer layer which occurs when the device is exposed to light. Photodiodes and photodetectors are disclosed in WO99/09603, GB2315594 and US5523555.

EXAMPLES

Synthesis of Trimer Precursor



To a solution of 2-tributyl stannyl thiophene (10.16 mL, 17.56 mmol), Amine 2 (7.18 g, 13.3 mmol) in toluene (80 mL) was added tetrakis (triphenylphosphine)palladium(0) (731 mg). The reaction mixture was refluxed for 4 hours and then the heat removed. The suspension was filtered through celite and evaporated to dryness. Recrystallisation from hexane afforded 3.98g (56%yield) of desired product. A further 1.16g was obtained from the mother liquor. Overall yield (73%). Structure was confirmed by GC-MS and ^1H NMR.

Synthesis of dibromo Trimer

To a solution of trimer precursor (3.97 g, 17.47 mmol) in DMF (40 mL) was added a solution of N-bromo succinimide (NBS) (2.66g, 14.94 mmol) in DMF (10 mL). The reaction mixture was stirred at room temperature for 30 mins. Monitored by GC-MS. A further 2.66g of NBS was added, this gave 100% of desired product by GC-MS. The reaction quenched by pouring the reaction mixture onto ice/ethanol. The product was filtered off and recrystallised from diethyl ether/ hexane affording, 5.19g (98% yield) of desired product.

Polymerisation of AB copolymer F8Trimer:

To a solution of 9,9-di-n-octylfluorene-2,7-di(ethyleneborate) (F8), (0.9267g, 1.75 mmol) and dibromo trimer (1.2290g, 1.75 mmol) in toluene (5 mL) was added dichlorobis(triphenylphosphine) palladium (II) 4mg in toluene (2.55 mL). The solution was degassed for 10 min then tetraethyl ammonium hydroxide (5.82 mL) was added. The reaction mixture was heated to 115 °C for 19h. End capping reagents were then added as follows, 0.3ml bromobenzene was added and allowed to react for 1 hour at a temperature of 115°C, then 0.3g phenylboronic acid was added and allowed to react for 1 hour at a temperature of 115°C. The reaction mixture was allowed to cool to room temperature and poured into 0.5l methanol. The polymer was obtained as a precipitate. 1.14g of polymer of mass 15K was obtained.

The present invention is described with reference to a number of specific embodiments, it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

Claims

1. Monomer having the formula



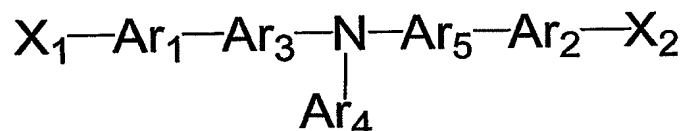
wherein the triarylamine unit comprises at least one nitrogen atom in the backbone of the monomer and at least three substituted or unsubstituted aryl or heteroaryl groups, said groups being the same or different,

wherein X_1 and X_2 are the same or different polymerisable groups,

wherein Ar_1 and Ar_2 are the same or different substituted or unsubstituted aryl or heteroaryl groups.

2. Monomer according to claim 1 wherein Ar_1 and Ar_2 are heteroaryl groups.
3. Monomer according to claim 2 wherein Ar_1 and Ar_2 are selected from the group comprising benzene, thiophene, pyrrole, furan and pyridine.
4. Monomer according to claim 1 wherein X_1 and X_2 are the same or different and are selected from the group comprising Cl, Br, I, boronic acids, boronic esters and boranes.
5. Monomer according to claim 4 wherein X_1 and X_2 are the same or different and are selected from the group comprising Br and boronic esters.
6. Monomer according to claim 1 wherein the triarylamine group comprises at least one heteroaryl group.
7. Monomer according to claim 6 wherein the triarylamine group comprises a triazine group.

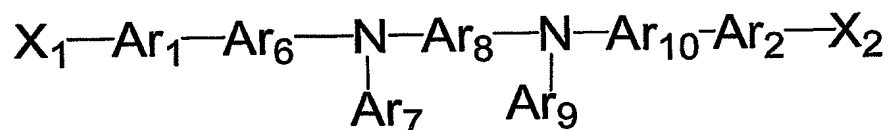
8. Monomer according to claim 1 wherein Ar_1 and Ar_2 are the same or different aryl or heteroaryl groups and are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.
9. Monomer according to claim 1 wherein the triarylamine comprises one nitrogen atom.
10. Monomer according to claim 1 wherein the triarylamine comprises two nitrogen atoms.
11. Monomer according to claim 9 having the structure



wherein X_1 and X_2 are the same or different polymerisable groups,

wherein Ar_1 , Ar_2 , Ar_3 , Ar_4 and Ar_5 are the same or different substituted or unsubstituted aryl or heteroaryl groups.

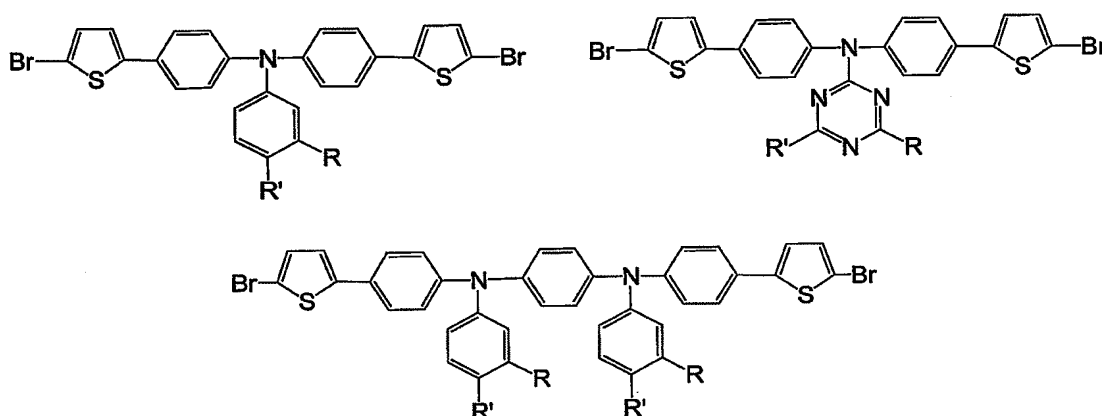
12. Monomer according to claim 11 wherein groups Ar_3 , Ar_4 and Ar_5 are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.
13. Monomer according to claim 10 having the structure



wherein X_1 and X_2 are the same or different polymerisable groups,

wherein $Ar_1, Ar_2, Ar_6, Ar_7, Ar_8, Ar_9, Ar_{10}$ are the same or different substituted or unsubstituted aryl or heteroaryl groups.

14. Monomer according to claim 13 wherein groups $Ar_6, Ar_7, Ar_8, Ar_9, Ar_{10}$ are substituted with moieties selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.
15. Monomers according to claim 1 having the structures



wherein R and R' are selected from the group comprising alkyl, perfluoroalkyl, alkylaryl, arylalkyl, heteroaryl, aryl, alkoxy, aryloxy and thioalkyl.

16. Polymer obtainable by the polymerisation of a monomer according to claim 1.
17. Copolymer obtainable by the polymerisation of a monomer according to claim 1 and one or more comonomers.
18. Copolymer according to claim 17 obtainable by the copolymerisation of a monomer according to claim 1 and one or more comonomers selected from the group comprising fluorenes, benzothiadiazoles, phenylenes, triaryl amines, stilbenes, quinoxalines, and biphenylenes.

19. Copolymer according to claim 18 obtainable by the copolymerisation of a monomer according to claim 1 and a comonomer selected from the group comprising fluorenes, benzothiadiazoles, triarylamine and phenylenes.
20. Optoelectronic device comprising a polymer according to claim 16 or a copolymer according to claim 17.
21. Optoelectronic device according to claim 20 wherein said device is an electroluminescent device.
22. Optoelectronic device according to claim 20 wherein said device is a photovoltaic device.
23. A process for preparing a polymer according to claim 16, which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and a monomer according to claim 1 having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX₃-anionic groups, wherein X is independently selected from the group consisting of F and OH.
24. A process for preparing a copolymer according to claim 17, which comprises polymerizing in a reaction mixture (a) a monomer according to claim 1 having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and one or more comonomers having at least two reactive halide functional groups; or (b) a monomer according to claim 1 having at least two reactive halide functional groups, and one or more comonomers having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group; or at least (c) a

monomer according to claim 1 having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group and one or more comonomers having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into-BX₃-anionic groups, wherein X is independently selected from the group consisting of F and OH.

INTERNATIONAL SEARCH REPORT

Int lional Application No
PCT/GB 02/04723

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G61/12 C07D333/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 66618 A (TOWNS CARL ROBERT ;DELL RICHARD O (GB); CAMBRIDGE DISPLAY TECH (GB) 13 September 2001 (2001-09-13) page 1; claim 1; examples 2-7 -----	1-24
A	WO 01 44769 A (SWANTECH L L C) 21 June 2001 (2001-06-21) cited in the application page 1; claims 1,6,10; example 3 -----	1-24
A	WO 01 49768 A (TOWNS CARL ROBERT ;DELL RICHARD O (GB); CAMBRIDGE DISPLAY TECH (GB) 12 July 2001 (2001-07-12) cited in the application page 1; claim 22 -----	1-24

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

9 January 2003

Date of mailing of the international search report

20/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Seelmann, I

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04723

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0166618	A	13-09-2001	AU 2385001 A	16-07-2001
			AU 3761801 A	17-09-2001
			EP 1246860 A1	09-10-2002
			EP 1263837 A1	11-12-2002
			WO 0149769 A1	12-07-2001
			WO 0166618 A1	13-09-2001
			AU 2690001 A	16-07-2001
			AU 3177700 A	04-10-2000
			AU 3577301 A	03-09-2001
			AU 3577801 A	03-09-2001
			EP 1169741 A1	09-01-2002
			EP 1244723 A2	02-10-2002
			EP 1263834 A1	11-12-2002
			EP 1257611 A1	20-11-2002
			WO 0149768 A2	12-07-2001
			WO 0162822 A1	30-08-2001
			WO 0162869 A1	30-08-2001
WO 0144769	A	21-06-2001	US 6351713 B1	26-02-2002
			EP 1250577 A1	23-10-2002
			WO 0144769 A1	21-06-2001
WO 0149768	A	12-07-2001	AU 2690001 A	16-07-2001
			EP 1244723 A2	02-10-2002
			WO 0149768 A2	12-07-2001
			AU 3177700 A	04-10-2000
			AU 3577301 A	03-09-2001
			AU 3577801 A	03-09-2001
			AU 3761801 A	17-09-2001
			EP 1169741 A1	09-01-2002
			EP 1263834 A1	11-12-2002
			EP 1257611 A1	20-11-2002
			EP 1263837 A1	11-12-2002
			WO 0162822 A1	30-08-2001
			WO 0162869 A1	30-08-2001
			WO 0166618 A1	13-09-2001